

952,156

# PATENT SPECIFICATION



NO DRAWINGS

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## COMPLETE SPECIFICATION

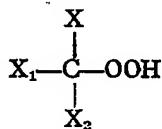
### Production of Chloroprene Polymers

- We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—
- This invention is directed to improvements in and relating to chloroprene (2-chloro-1,3-butadiene) polymers.
- The term "chloroprene polymers" means homopolymers of chloroprene and copolymers of chloroprene with up to 10 per cent by weight, based on total monomer content, of other monomers containing the group
- $\text{CH}_2=\text{C}-$ , e.g., vinyl substituted aromatic compounds, such as styrene, vinyltoluenes and vinylnaphthalenes; acrylic and methacrylic acid esters and nitriles, such as methyl methacrylate and acrylonitrile; and conjugated diolefinic compounds such as 1,3-butadiene, isoprene, and 2,3-dichloro-1,3-butadiene. It is preferred that chloroprene be polymerized with no other copolymerizable monomer present in order to obtain products having good tensile strength.
- Low-molecular-weight chloroprene polymers of relatively low viscosity prepared by polymerizing chloroprene in the presence of a sufficient amount of a dialkyl xanthogen disulfide are especially useful as plasticizers for higher-molecular-weight chloroprene polymers because they can be co-cured therewith. However, it is important that these low-viscosity polymers themselves cure to vulcanizates having good tensile properties if the tensile properties of the polymers into which they are incorporated are not to be adversely affected. The polymerization of chloroprene to low-molecular-weight polymers in the presence of dialkyl xanthogen disulfides as modifying agents must be carried out under carefully controlled conditions if the resulting vulcanizates are to have satisfactory tensile strength. Since the dialkyl xanthogen disulfides tend to retard polymerization, it is difficult to initiate and maintain polymerization under these conditions using conventional initiation techniques.
- According to the present invention there is provided a process for preparing chloroprene polymers in an aqueous emulsion in the presence of a dialkyl xanthogen disulfide, the alkyl groups contain from 1 to 8 carbon atoms, which comprises using the dialkyl xanthogen disulfide in amounts from 0.01 to 0.04 part mole, per 100 parts by weight of monomer, at a temperature of from 15 to 25° C., a pH of from 5 to 11, and in the presence of a catalyst system comprising per 100 parts by weight of monomer,
- (a) between 0.00065 to 0.0013 part mole of an organic hydroperoxide,
- (b) between 0.1 to 0.3 part by weight of an inorganic water-soluble persulfate, and
- (c) at least 0.05 part by weight of an inorganic water-soluble hydrosulfite and/or pyrosulfite, with the proviso that (a) and (b) are added separately to the polymerization system before polymerization is initiated, polymerization then being initiated and maintained by the addition of (c).
- The term "part mole" means that the molecular weight of the particular disulfide used is calculated in the same units as the amounts of monomer. In other words, if the parts of monomer used are calculated in terms of grams or pounds, the molecular weight of the disulfide is calculated in terms of grams or pounds and from about 1 per cent to 4 per cent of this amount of disulfide is used.
- The dialkyl xanthogen disulfides have the formula
- $$\begin{array}{c} \text{R}_1-\text{O}-\text{C}-\text{S}-\text{S}-\text{C}-\text{O}-\text{R}_2 \\ | \qquad \qquad \qquad || \\ \text{S} \qquad \qquad \qquad \text{S} \end{array}$$

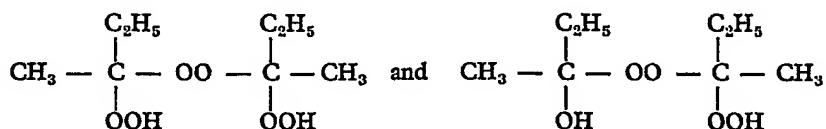
[P<sub>1</sub>] [ ]

in which R<sub>1</sub> and R<sub>2</sub> are alkyl groups containing from one to eight carbon atoms, preferably three to four carbon atoms. At least about 0.01 part mole is required to obtain a low-molecular-weight polymer such as is useful as a plasticizing agent for more solid polymers. If more than about 0.04 part mole is used, resulting vulcanizates tend to have unsatisfactory tensile strength. The preferred amount is about 0.015 to 0.025 part mole.

Any suitable organic hydroperoxide may be employed in the catalyst system. Of particular value are the organic hydroperoxides which contain from 4 to 21 carbon atoms. A representative class of hydroperoxides is the tertiary organic hydroperoxides which correspond to the formula



wherein X, X<sub>1</sub> and X<sub>2</sub> are independently



It is to be understood that mixtures of these peroxides may be used. At least about 0.00065 part mole of the hydroperoxide, per 100 parts by weight of monomer is required for polymerization to be initiated by the catalyst system. If more than about 0.0013 part mole is used, the polymerization proceeds too rapidly to be controlled.

The water-soluble inorganic persulfates that may be used are preferably the sodium, potassium, or ammonium salts of persulfuric acid. Mixtures of these persulfates may be used. The polymerization proceeds too slowly when less than 0.1 part is used and the polymerization is difficult to control when more than 0.3 part is used.

Component (c) of the catalyst system is a water-soluble inorganic hydrosulfite or water-soluble inorganic pyrosulfite or mixtures thereof. Because of their ready availability, the sodium salts are preferred. Sodium hydrosulfite (also called sodium dithionite) is available as the dihydrate (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> · 2H<sub>2</sub>O). The amount of at least 0.05 part by weight to be used refers to the anhydrous material. Sodium pyrosulfite (also called sodium metabisulfite) has the formula Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>. The quantity of this component will vary somewhat depending on the activity of individual amounts of monomer. In general, at least a total of about 0.05 part by weight, per

selected from the group consisting of aliphatic acyclic, aliphatic cyclic, aryl, alkaryl and aralkyl radicals, with the proviso that two or three of the X's together with the carbon atom attached to the hydroperoxy group may be joined to form a ring system containing from 1 to 2 rings with each ring containing from 5 to 6 carbon atoms and with the further proviso that the carbon atom directly attached to the hydroperoxy group is not part of an aromatic ring. Examples of suitable organic hydroperoxides include cumene hydroperoxide, (z,z-dimethylbenzyl hydroperoxide), tert-butyl hydroperoxide, diisopropylbenzene hydroperoxide, pinane hydroperoxide, methane hydroperoxide (which is the hydroperoxide of 1-isopropyl-4-methyl cyclohexane) and p-dodecyl-z,z-dimethylbenzyl hydroperoxide. Another group of suitable hydroperoxides is the ketone peroxides such as cyclohexanone peroxide and methyl ethyl ketone peroxide. Methyl ethyl ketone peroxide, for example, is a mixture consisting predominantly of

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100 parts by weight of monomer, is required to initiate and maintain polymerization at a satisfactory rate. The preferred range is from about 0.06 to about 0.12 part. A preferred method is to initiate polymerization by adding 50 to 90 per cent of the salt all at once and then to maintain polymerization at the desired rate by gradual addition of the salt as required.

The polymerization is carried out in aqueous emulsion using any of the conventional emulsifying agents used in chloroprene polymerizations, including water-soluble salts of compounds of the following types: long-chain fatty acids; dimerized fatty acids, rosins and modified rosins or partially polymerized rosins; fatty alcohol sulfates; and arylsulfonic acids or formaldehyde condensates thereof, such as nonylbenzene sulfonic acid or the formaldehyde condensation product of naphthalenesulfonic acid.

It has been found that the dialkyl xanthogen disulfides act most effectively when the pH of the polymerization system is between about 5 and 11, since otherwise the polymers produced tend to have too high a viscosity to be satisfactory for use as plasticizers for more solid polychloroprenes. The preferred pH range is about 6 to 10.

As has been mentioned, the temperature should be in the range of 15° C. to 25° C.

- Below about 15° C. polymerization is inconveniently slow. Above about 25° C. the polymers prepared cure to vulcanizates having poorer tensile strength.
- 5 In practicing the process of this invention, an aqueous emulsion may be prepared, by conventional techniques, containing the monomer, the dialkyl xanthogen disulfide, the emulsifying agent, and water. The monomer content of the aqueous emulsion is not critical, but usually ranges from 30 to 60 per cent by weight of the total weight of the emulsion. It is usually convenient to incorporate the organic hydroperoxide into the aqueous emulsion of the monomer. As usual in chloroprene polymerizations, oxygen is excluded from the atmosphere above the polymerization medium. This may be done conveniently by sweeping the reaction vessel with a stream of an inert gas, such as nitrogen, and maintaining a nitrogen atmosphere over the polymerization medium. The temperature is adjusted by conventional methods to about 15 to 25° C.
- 10 To the monomer emulsion is then added the persulfate, preferably as a water emulsion. Optionally, this water solution may contain also a small amount of the sodium salt of 2-anthraquinonesulfonate. This is not an essential part of this invention but merely provides an additional activation to allow for possible variations in activity of individual lots of monomer.
- 15 Polymerization is then initiated by addition of the hydrosulfite or pyrosulfite. This salt
- may be added initially either as a solid or as an aqueous solution. To maintain the desired polymerization rate, subsequent amounts are conveniently added in the form of an aqueous solution.
- 20 When the desired monomer conversion has been attained, polymerization is stopped in the usual manner by adding conventional short-stopping agents, for example, as described in U.S. Patent 2,576,009. If desired, unreacted monomer may be removed by known methods, for example, as described in U.S. Patent 2,467,769. The polymer may be isolated by known techniques such as by drum drying, as described in British Specification 807,496 or by coagulation of the solid polymer and separation from the aqueous phase.
- 25 When the polymers of this invention are first isolated they are quite fluid, with Brookfield viscosities at 60° C. in the range of about 350,000 to 1,200,000 centipoises. However, they crystallize rapidly and in a day or two they have become crumbly, elastic solids having a fractice-like consistency. However, they can be returned to their fluid state by warming at 60° C. Using conventional polychloroprene curing methods, they may be cured to vulcanizates having excellent tensile strength. These properties make them eminently suitable for use as plasticizing agents for more solid chloroprene polymers.
- 30 The following Examples further illustrate the invention; parts are by weight unless otherwise indicated.

## EXAMPLE 1

An emulsion is prepared using the following recipe:

	Parts
Chloroprene	100
Diisopropyl xanthogen disulfide	4.7 (0.017 part mole)
Oleic acid	3.8
α,α-Dimethylbenzyl hydroperoxide (cumene hydroperoxide)	0.14 (0.0092 part mole)
Sodium hydroxide	0.24
Water	133.33

- Emulsification is effected by mixing the chloroprene, the diisopropyl xanthogen disulfide, the oleic acid, and the cumene hydroperoxide, and emulsifying this mixture with the water solution of the sodium hydroxide. Emulsification is effected under nitrogen. The pH of the system is 9. An atmosphere of nitrogen is maintained in the polymerization vessel and mild agitation is maintained throughout the polymerization process.
- To the emulsion so prepared is added a solution of the following composition:

Parts	
Ammonium persulfate	0.20
Sodium 2-anthraquinone sulfonate	0.006
Water	5.0

- Up to this time no polymerization has taken place. Polymerization is now initiated by adding 0.067 part by weight (based on 5 100 parts by weight of chloroprene) of solid sodium hydrosulfite dihydrate to the system (0.056 part on an anhydrous basis). Thereafter, polymerization is maintained by the addition, as needed, of a solution containing 0.01 part by weight of sodium hydrosulfite dihydrate, 0.0002 part of sodium hydroxide, and 0.23 part of water. The rate of polymerization is such as to give an increase in specific gravity of about 0.005 10 g./cc. per minute.
- Polymerization is stopped when the specific 15 gravity of the latex is 1.063 at 20° C. (a chloroprene conversion of 82 per cent) by addition of 0.015 part of phenothiazine and 20 0.015 part of 4-tert-butylcatechol dissolved in toluene and emulsified in water containing

as emulsifying agents the sodium salt of a formaldehyde-naphthalenesulfonic acid condensate and sodium lauryl sulfate.

The polymer is isolated by drum drying, which is carried out on an 8-inch chromium-plated, double drum drier, using a drum speed of 20 r.p.m. and a steam pressure of 80 p.s.i.g. The latex is introduced continuously into the nip between the rolls. The polymer is removed from the rolls by "doctor knives."

The polymer, when first isolated, is a fluid having a Brookfield viscosity at 60° C. of about 470,000 cps. However, it crystallizes rapidly and in two days it has become a crumbly, elastic, solid having a factice-like consistency. It can be returned to its fluid state by warming to 60° C.

The polymer is compounded using the following recipe:

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Parts	
Polymer	100
N-Phenyl-2-naphthylamine	2
Intermediate Super Abrasion Furnace Black	10
Magnesium oxide	4
Zinc oxide	10
Di-o-tolylguanidine	3
Monoethanolamine	4.1

- Cure is effected by heating at 152° C. for five minutes in an open mold and for fifteen minutes in a closed mold under a pressure of 445 p.s.i. The tensile properties, measured by ASTM Method D 412—51 T, are:

Diethyl xanthogen disulfide.  
Dibutyl xanthogen disulfide.  
Bis (2-ethylhexyl) xanthogen disulfide.

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#### EXAMPLES 2 AND 3.

Polymerizations are carried out as described in Example 1 except that different amounts of diisopropyl xanthogen disulfide are used. The polymers are compounded and cured as described in Example 1 except that the compounding recipe contains 20 parts of easy processing channel black instead of 10 parts of intermediate super abrasion furnace black.

The following table summarizes the data:

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- Modulus at 400% elongation, p.s.i. 1450  
Tensile strength at the break, p.s.i. 2170  
Elongation at the break, % 505

- 50 Similar results are obtained when the diisopropyl xanthogen disulfide is replaced by one of the following:

Example	Diisopropyl xanthogen disulfide		Brookfield viscosity at 60° C. of isolated polymer	Tensile strength at break of cured polymer
	Parts	Part Moles	cps.	p.s.i.
2	5.0	0.0185	450,000	2100
3	5.4	0.020	350,000	2100

**EXAMPLES 4—6.**

Polymerizations are carried out as described in Example 1 except that in each example 5 an equimolar amount of a different peroxide

(0.00092 part mole) is used instead of cumene hydroperoxide. The polymerization proceeds as described in Example 1. The following hydroperoxides are used:

Example	Hydroperoxide	Brookfield Viscosity
		at 60° C. of freshly isolated polymer
10	4 diisopropylbenzene hydroperoxide	630,000
	5 pinane hydroperoxide	470,000
	6 methyl ethyl ketone peroxide	1,160,000

**EXAMPLE 7.**

A polymerization is carried out as described in Example 1 except that sodium pyrosulfite is used instead of sodium hydrosulfite. Polymerization is initiated by adding 0.067 part by weight of sodium pyrosulfite. Polymerization is thereafter maintained by the addition, as needed, of a solution containing 0.01 part of sodium pyrosulfite, 0.0002 part of sodium hydroxide, and 0.23 part of water. The isolated polymer has a Brookfield viscosity at 60° C. of 600,000.

The polymer is compounded and cured as described in Example 1 except that medium thermal carbon black is used instead of the intermediate super abrasion furnace black. The tensile strength at the break of the cured polymer is 2400 p.s.i. (ASTM Method D 412—51 T).

**WHAT WE CLAIM IS:—**

1. A process for preparing chloroprene polymers in an aqueous emulsion in the presence of a dialkyl xanthogen disulfide, the alkyl groups containing 1 to 8 carbon atoms, which comprises using the dialkyl xanthogen disulfide in amounts from 0.01 to 0.04 part mole per 100 parts of monomer, at a temperature of from 15° C. to 25° C., a pH of from 5 to 11, and a catalyst system comprising, per 100 parts by weight of monomer,
  - (a) between 0.00065 to 0.0013 part mole of an organic hydroperoxide,
  - (b) between 0.1 to 0.3 part by weight of an inorganic water-soluble persulfate, and

(c) at least 0.05 part by weight of an inorganic water-soluble hydrosulfite and/or pyrosulfite; with the proviso that (a) and (b) are added separately to the polymerization system before polymerization is initiated, polymerization then being initiated and maintained by the addition of (c).

2. A process according to Claim 1 wherein the chloroprene polymer is a homopolymer of chloroprene.

3. A process according to Claim 1 or 2 wherein the dialkyl xanthogen disulfide is diisopropyl xanthogen disulfide.

4. A process according to any of Claims 1 to 3 wherein the organic hydroperoxide contains from 4 to 21 carbon atoms.

5. A process according to Claim 4 wherein the organic hydroperoxide is  $\alpha,\omega$ -dimethylbenzyl hydroperoxide.

6. A process according to any of Claims 1 to 5 wherein component (c) is sodium hydrosulfite.

7. A process according to any of Claims 1 to 5 wherein component (c) is sodium pyrosulfite.

8. A process according to any of Claims 1 to 7 wherein the inorganic water-soluble persulfate is ammonium persulfate.

9. A process according to any of Claims 1 to 8 wherein the water-soluble persulfate is added in an aqueous solution.

10. A process according to Claim 9 wherein the aqueous persulfate solution contains the

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sodium salt of 2-anthraquinonesulfonate.

11. The process substantially as hereinbefore described.

5 12. The process substantially as described in any of the foregoing Examples.

13. Chloroprene polymers whenever prepared according to the process of any of the preceding claims.

14. Cured chloroprene polymers prepared from chloroprene polymers obtained according to Claim 11. 10

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For the Applicants.

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